

CLAIMS

1. Material capable of being obtained by the sol-gel route comprising:

(a) at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides,

(b) at least one organic UV-A sunscreen agent having a maximum absorption wavelength of less than 370 nm,

(c) at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer,

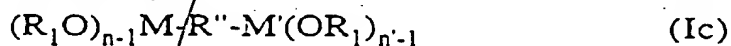
(d) at least one solvent, and

(e) an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation,

said material having a maximum absorption wavelength ( $\lambda_{max}$ ) which is situated in the range from 370 to 400 nm.

2. Material according to Claim 1, characterized in that the metal alkoxide is chosen from the group composed of:

(1) metalloorganic compounds corresponding to one of the following formulae:



in which:

M and M' represent, independently of one another, a zirconium, titanium or aluminum atom,

n and n' denote the respective valencies of the metal atoms represented by M and M',

R<sub>1</sub> represents a saturated or unsaturated and linear or

branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, sulfur, oxygen or phosphorus atom, and more preferably a linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, alkyl group,

5 R and R' represent, independently of one another, a saturated or unsaturated and linear, branched or cyclic C<sub>1-30</sub>, preferably C<sub>2-20</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or

10 branched alkyl group, a cycloalkyl group or an aryl group,

it being possible for said R and R' groups to be substituted by groups capable of reacting with the organic or silicone polymer and it being possible for

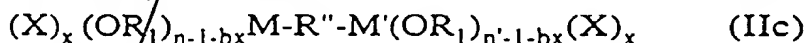
15 said R and R' groups to additionally comprise a cosmetically or dermatologically active group,

R'' represents a saturated or unsaturated and linear, branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen,

20 phosphorus, sulfur or oxygen atom, such as, for example, a linear or branched alkylene group, a cycloalkylene group or an arylene group, it being possible for said R'' group to be substituted by groups capable of reacting with the organic or silicone polymer and it being

25 possible for said R'' group additionally to comprise a cosmetically or dermatologically active group;

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



in which:

30 M, M', n, n', R<sub>1</sub>, R, R' and R'' have the same meanings as

those given for the above formulae (Ia) to (Id),  
X represents a monodentate ligand or a chelating group  
comprising a nitrogen atom, a phosphorus atom, a sulfur  
atom or an oxygen atom which can be covalently bonded to  
5 a group capable of reacting with said functionalized  
organic polymer or said functionalized silicone polymer  
(c), and which can comprise a cosmetically or  
dermatologically active group,

x represents the number of X ligands; and

10 b represents the number of bonding atoms of the X ligand.

3. Material according to Claim 2, characterized in  
that said group capable of reacting with the  
functionalized organic polymer or the functionalized  
silicone polymer (c) carried by the R, R' or R'' group  
15 and/or by the X ligand can be chosen from halogen atoms,  
the hydroxyl, acyl, carboxyl, ester, thiol,  
alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido,  
thioureido, urethane, imidazolo, morpholino or pyrrolo  
groups, groups comprising ethylenic unsaturation, such as  
20 the (meth)acrylic and vinyl groups, halogenated groups,  
such as perfluorinated groups, hydroxylated or  
carboxylated groups, phosphonic, phosphonate, phosphate,  
pyrophosphate, phosphonium, sulfonate, amine, quaternary  
ammonium, amide, amino acid and polypeptide groups, the  
25 acetic acid, acetoacetate (ACAC) or ethyl acetoacetate  
group, or a group deriving from EDTA and its derivatives.

4. Material according to Claim 2 or 3, characterized  
in that the monodentate or polydentate ligand X is chosen  
from sulfuric acids, sulfonic acids, phosphonic acids,  
30 phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones,  
esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids,  
preferably  $\alpha$ - or  $\beta$ -hydroxylated amino acids, and their  
derivatives,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and  
polyethers, imines, optionally hydroxylated amides, azo  
35 compounds, thiols, ureas, thioether sulfoxides, thioether  
sulfones, optionally cyclic thioethers, di(thioethers),

monoalcohols or polyols, dextrin and its derivatives, or thiazolidines.

5. Material according to any one of the preceding claims, characterized in that the metal alkoxide is  
5 chosen from tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

6. Material according to any one of the preceding claims, characterized in that the metal alkoxide is  
10 present in an amount ranging from 0.1% by weight to 99% by weight, preferably from 0.5% to 80% by weight, with respect to the total weight of the material.

7. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen  
15 agent is chosen from:

- dibenzoylmethane derivatives,
- camphor derivatives,
- benzimidazole derivatives,
- benzoxazole derivatives,
- 20 - benzophenone derivatives,
- silane or polyorganosiloxane derivatives comprising benzophenone group(s),
- anthranilates, and
- their mixtures.

8. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen  
25 agent is chosen from:

- 2-methyldibenzoylmethane,
- 4-methyldibenzoylmethane,
- 30 - 4-isopropyldibenzoylmethane,
- 4-tert-butyldibenzoylmethane,
- 2,4-dimethyldibenzoylmethane,
- 2,5-dimethyldibenzoylmethane,
- 4,4'-diisopropyldibenzoylmethane,
- 35 - 4,4'-dimethoxydibenzoylmethane,
- 4-tert-butyl-4'-methoxydibenzoylmethane,

- 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,
- 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane,
- 2,4-dimethyl-4'-methoxydibenzoylmethane,
- 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

9. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen agent is 4-tert-butyl-4'-methoxydibenzoylmethane.

10. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen agent is present in an amount ranging from 0.1% by weight to 60% by weight, preferably from 0.1% to 30% by weight, with respect to the total weight of the material.

11. Material according to any one of the preceding claims, characterized in that the functionalized organic or silicone polymer is a homopolymer or random, block and/or graft copolymer chosen from:

- (a) alkyloxazoline homopolymers and copolymers;
- (b) homopolymers and copolymers of (meth)acrylic acid, of crotonic acid, of maleic acid, of itaconic acid, of styrenesulfonic acid, of 2-(acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid and/or of vinylphosphonic acid;
- (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl

esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;

(f) polyethers;

10 (g) polyesters;

(h) homopolymers and copolymers of olefins or of cycloolefins;

(i) polyamides and polyesteramides;

15 (j) polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;

(k) fluoropolymers;

(l) natural polymers and modified natural polymers;

(m) polyorganosiloxanes;

20 (n) polyorganophosphazenes;

(o) polysilanes, polycarbosilanes or polysilazanes; and

(p) mixtures of these polymers.

12. Material according to any one of the preceding claims, characterized in that the functionalized organic or silicone polymer is chosen from poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s, poly(amy1 [sic] alcohol) and poly(vinylpyrrolidone).

30 13. Material according to Claim 12, characterized in that the functionalized organic or silicone polymer is a polydimethylsiloxane-diol.

14. Material according to any one of the preceding claims, characterized in that the functionalized organic or silicone polymer is present in an amount ranging from 35 0.1% by weight to 99% by weight, preferably from 0.5% to

80% by weight, with respect to the total weight of the material.

15. Material according to any one of the preceding claims, characterized in that the solvent is an alcohol.

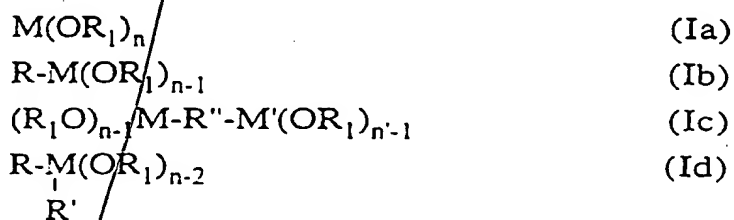
5 16. Material according to Claim 15, characterized in that the alcohol is a linear or branched lower alcohol.

17. Material according to Claim 16, characterized in that the alcohol is ethanol.

10 18. Process for shifting the maximum absorption wavelength ( $\lambda_{\max}$ ) of an organic UV-A sunscreen agent having a  $\lambda_{\max}$  of less than 370 nm into the range from 370 to 400 nm, characterized in that it comprises the combination of this screening agent with a sol comprising at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer, at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides, at least one solvent and an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation.

15 19. Process according to Claim 18, characterized in that the metal alkoxide is chosen from the group composed of:

20 25 (1) metalloorganic compounds corresponding to one of the following formulae:

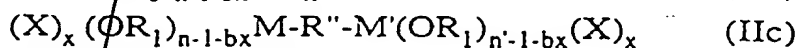


in which:

M and M' represent, independently of one another, a zirconium, titanium or aluminum atom,

30 n and n' denote the respective valencies of the metal

atoms represented by M and M',  
R<sub>1</sub> represents a saturated or unsaturated and linear or  
branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, hydrocarbonaceous group  
optionally comprising a heteroatom, such as a nitrogen,  
5 sulfur, oxygen or phosphorus atom, and more preferably a  
linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, alkyl group,  
R and R' represent, independently of one another, a  
saturated or unsaturated and linear, branched or cyclic  
C<sub>1-30</sub>, preferably C<sub>2-20</sub>, hydrocarbonaceous group optionally  
10 comprising a heteroatom, such as a nitrogen, phosphorus,  
sulfur or oxygen atom, such as, for example, a linear or  
branched alkyl group, a cycloalkyl group or an aryl  
group,  
it being possible for said R and R' groups to be  
15 substituted by groups capable of reacting with the  
organic or silicone polymer and it being possible for  
said R and R' groups to additionally comprise a  
cosmetically or dermatologically active group,  
R'' represents a saturated or unsaturated and linear,  
20 branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group  
optionally comprising a heteroatom, such as a nitrogen,  
phosphorus, sulfur or oxygen atom, such as, for example,  
a linear or branched alkylene group, a cycloalkylene  
group or an arylene group, it being possible for said R''  
25 group to be substituted by groups capable of reacting  
with the organic or silicone polymer and it being  
possible for said R'' group additionally to comprise a  
cosmetically or dermatologically active group;  
(2) complexed or chelated metalloorganic compounds  
30 corresponding to one of the following formulae:





in which:

M, M', n, n', R<sub>1</sub>, R, R' and R'' have the same meanings as those given for the above formulae (Ia) to (Id),

X represents a monodentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic polymer or said functionalized silicone polymer (c), and which can comprise a cosmetically or dermatologically active group,

x represents the number of X ligands; and

b represents the number of bonding atoms of the X ligand.

20. Process according to Claim 19, characterized in that said group capable of reacting with the functionalized organic polymer or the functionalized silicone polymer (c) carried by the R, R' or R'' group and/or by the X ligand can be chosen from halogen atoms, the hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino or pyrrolo groups, groups comprising ethylenic unsaturation, such as the (meth)acrylic and vinyl groups, halogenated groups, such as perfluorinated groups, hydroxylated or carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives.

21. Process according to Claim 19 or 20, characterized in that the monodentate or polydentate ligand X is chosen from sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids, preferably  $\alpha$ - or  $\beta$ -hydroxylated amino acids, and their derivatives,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and polyethers, imines, optionally

hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, optionally cyclic thioethers, di(thioethers), monoalcohols or polyols, dextrin and its derivatives, or thiazolidines.

5 22. Process according to any one of Claims 18 to 21, characterized in that the metal alkoxide is chosen from tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

10 23. Process according to any one of Claims 18 to 22, characterized in that the organic UV-A sunscreen agent is chosen from:

- dibenzoylmethane derivatives,
- camphor derivatives,
- benzimidazole derivatives,
- 15 - benzoxazole derivatives,
- benzophenone derivatives,
- silane or polyorganosiloxane derivatives comprising benzophenone group(s),
- anthranilates, and
- 20 - their mixtures.

24. Process according to any one of Claims 18 to 23, characterized in that the organic UV-A sunscreen agent is chosen from:

- 2-methyldibenzoylmethane,
- 25 - 4-methyldibenzoylmethane,
- 4-isopropyldibenzoylmethane,
- 4-tert-butyldibenzoylmethane,
- 2,4-dimethyldibenzoylmethane,
- 2,5-dimethyldibenzoylmethane,
- 30 - 4,4'-diisopropyldibenzoylmethane,
- 4,4'-dimethoxydibenzoylmethane,
- 4-tert-butyl-4'-methoxydibenzoylmethane,
- 2-methyl-5-isopropyl-4'-methoxydibenzoyl-methane,
- 35 - 2-methyl-5-tert-butyl-4'-methoxydibenzoyl-methane,

- 2,4-dimethyl-4'-methoxydibenzoylmethane,
- 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

25. Process according to any one of Claims 18 to 24,  
5 characterized in that the organic UV-A sunscreen agent is  
4-tert-butyl-4'-methoxydibenzoylmethane.

26. Process according to any one of Claims 18 to 25,  
characterized in that the functionalized organic or  
silicone polymer is a homopolymer or random, block and/or  
10 graft copolymer chosen from:

- (a) alkyloxazoline homopolymers and copolymers;
- (b) homopolymers and copolymers of (meth)acrylic acid,  
of crotonic acid, of maleic acid, of itaconic acid,  
of styrenesulfonic acid, of 2-  
15 (acrylamido)methylpropanesulfonic acid, of 2-  
sulfoethyl methacrylate, of vinylsulfonic acid  
and/or of vinylphosphonic acid;
- (c) homopolymers of acrylic or methacrylic esters or  
amides and their copolymers with comonomers chosen  
20 from unsaturated carboxylic acids, sulfonic acids,  
phosphonic acids, vinyl esters and ethers, olefins,  
styrene, substituted styrenes, fluoro- and  
perfluoroolefins, perfluoroalkyl (meth)acrylates,  
fluorovinyl compounds and unsaturated organosilanes,  
25 organosiloxanes or organopolysiloxanes;
- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl  
esters or amides and their copolymers with  
comonomers chosen from unsaturated carboxylic acids,  
30 sulfonic acids, phosphonic acids, vinyl esters and  
ethers, olefins, styrene, substituted styrenes,  
fluoro- and perfluoroolefins, perfluoroalkyl  
(meth)acrylates, fluorovinyl compounds, and  
unsaturated organosilanes, organosiloxanes or  
35 organopolysiloxanes;
- (f) polyethers;

- (g) polyesters;
- (h) homopolymers and copolymers of olefins or of cycloolefins;
- (i) polyamides and polyesteramides;
- 5 (j) polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;
- (k) fluoropolymers;
- (l) natural polymers and modified natural polymers;
- 10 (m) polyorganosiloxanes;
- (n) polyorganophosphazenes;
- (o) polysilanes, polycarbosilanes or polysilazanes; and
- (p) mixtures of these polymers.

27. Process according to any one of Claims 18 to 26,  
15 characterized in that the functionalized organic or silicone polymer is chosen from poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s,  
20 poly(amyl [sic] alcohol) and poly(vinylpyrrolidone).

28. Process according to Claim 28, characterized in that the functionalized organic or silicone polymer is a polydimethylsiloxane-diol.

29. Process according to any one of Claims 18 to 28,  
25 characterized in that the solvent is a linear or branched lower alcohol.

30. Process according to Claim 29, characterized in that the alcohol is ethanol.

31. Process according to any one of Claims 18 to 30,  
30 characterized in that the metal alkoxide is mixed with a solution of functionalized organic or silicone polymer before the addition of the screening agent.

32. Cosmetic and/or dermatological composition, characterized in that it comprises, in a cosmetically  
35 and/or dermatologically acceptable vehicle, an effective amount of the material according to any one of Claims 1

to 17.

33. Cosmetic and/or dermatological composition according to Claim 32, characterized in that the material is in the form of particles obtained by drying and milling.

34. Cosmetic and/or dermatological composition according to Claim 32 or 33, characterized in that the effective amount of the material according to any one of Claims 1 to 17 lies within the range from 1% by weight to 99% by weight with respect to the total weight of the cosmetic and/or dermatological composition.

35. Cosmetic and/or dermatological composition according to any one of Claims 32 to 34, characterized in that the effective amount of the material according to any one of Claims 1 to 17 lies within the range preferably from 5 to 60% by weight with respect to the total weight of the cosmetic and/or dermatological composition.

36. Cosmetic and/or dermatological composition according to any one of Claims 32 to 35, characterized in that the mean size of the particles obtained by drying and milling the material according to any one of Claims 1 to 17 lies within the range from 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$ .

37. Cosmetic and/or dermatological composition according to Claim 36, characterized in that the mean size of the particles obtained by drying and milling the material according to any one of the Claims 1 to 17 lies within the range from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

38. Cosmetic and/or dermatological composition according to any one of Claims 32 to 37, characterized in that an additive chosen from sunscreen agents other than organic UV-A sunscreen agents, agents for the artificial tanning and/or browning of the skin, pigments, fatty substances, organic solvents, thickeners, softeners or antioxidants can additionally be added.

add  
a'